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ENVIRONMENTAL APPLICATIONS OF ADVANCED INSTRUMENTAL ANALYSIS: ASSISTANCE PROJECTS FY 74

Ann L. Alford

Southeast Environmental Research Laboratory
Athens, Georgia

June 1975

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16. ABSTRACT

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This report was submitted in fulfillment of Project 16020 GHZ by the Southeast Environmental Research Laboratory, Athens, Georgia. Projects discussed were completed during FY 1974.

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By

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ABSTRACT

The Analytical Chemistry Branch of the Southeast Environmental Research Laboratory identified and measured aquatic pollutants under seven projects in answer to requests for assistance from other EPA organizations and other government agencies. In most cases these analyses helped to solve, or at least to understand more clearly, the related pollution incident and in some cases provided evidence for enforcement of regulatory legislation. Under an additional project, analytical consultations were held as requested by various organizations concerned with pollution incidents.

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CONTENTS

Sections		Page
I	Recommendations	1
II	Introduction	2
III	Discussion	3
	1. Elemental Analyses to Assess Environmental Impact of Pesticide Plant Explosion and Fire	3
	2. Chemical Elements in Water from Sugar Beet Wastewater Holding Ponds	7
	3. Chemical Elements in Waste Plating Solution	9
	4. Elemental Composition of a Major Component of Ore Processing Plant Tailings	11
	5. Chemical Elements and Volatile Organic Compounds in Landfill Leachate	14
	6. Taste and Odor Problems in Well Waters	19
	a. Municipal Well	19
	b. Private Well	22
	7. Vinyl Chloride in Water	23
	a. Analytical Method	23
	b. Loss Mechanisms	25
	8. Dissemination of Analytical Information	26
	a. Consultations	26
	b. Symposium	27
IV	References	28
V	Glossary of Abbreviations	30

TABLES

No.		Page
1	Elements Detected by SSMS in Plant Yard Ash and Related Samples	4
2	Mercury and Arsenic in Ash Samples Analyzed by Neutron Activation	6
3	Elements Detected in Holding Pond and Ground Water Samples	8
4	Elements Detected in Waste Plating Solution	10
5	Major Elemental Components of Cummingtonite	12
6	Minor Elemental Components of Cummingtonite	13
7	Volatile Organic Material in Well Water Samples	17
8	Volatile Organic Compounds Identified in Well Water Samples from Landfill Area	18
9	Elements Detected in Well Water Samples from Landfill Area	20
10	Vinyl Chloride in Industrial Effluent Samples	24

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SECTION I

RECOMMENDATIONS

Existing analytical techniques should be continually improved, and new techniques should be investigated for applicability to pollutant analysis. Information about specific pollution incidents should be widely disseminated to help solve and perhaps prevent future environmental problems.

SECTION II

INTRODUCTION

The Analytical Chemistry Branch* (ACB) at the Southeast Environmental Research Laboratory (SERL) develops techniques for identifying and quantifying chemical pollutants, and identifies specific compounds associated with various pollution sources. The ACB has analyzed many samples related to a variety of specific pollution problems. Analytical results were reported only to the persons who requested the analyses and therefore had limited distribution. Earlier problems studied by the ACB have been summarized in annual reports[1,2,3] to acquaint other researchers and administrators with the type of information that can be obtained and to inform environmental chemists of technique applications and developments. This report summarizes fiscal year 1974 projects.

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*Formerly the National Water Contaminants Characterization Research Program.

SECTION III

DISCUSSION

1. ELEMENTAL ANALYSES TO ASSESS ENVIRONMENTAL IMPACT OF PESTICIDE PLANT EXPLOSION AND FIRE

An explosion and ensuing fire that completely destroyed a pesticide formulation plant and warehouse in Oklahoma prompted the EPA's investigation of the environmental impact of the incident on the area receiving ash and debris. Samples of ash, water, and grass were obtained by state officials who requested analyses by EPA laboratories. The plant and warehouse contained several toxic materials when the explosion occurred, and a large area received ash and debris that could have contaminated receiving water and soil. Information from the Oklahoma State Health Department indicated that arsenic, mercury, and phosphorus compounds were among the pesticides in the plant.

The EPA's Region VI Surveillance and Analysis Division, which was responsible for assessing the environmental effects, requested the SERL's assistance. The SERL provided analytical standards of pesticides, advice on analytical methodology, and elemental analyses by spark source mass spectrometry (SSMS) and neutron activation (NAA).

Five samples were collected and shipped to the SERL:

- ash from the plant yard,
- airborne ash from an area 3.3 miles northeast (downwind) of the plant,
- grass from an area 0.25 mile northeast of the plant,
- roadside water from an area one mile northeast of the plant, and
- control water from Lake Lugert, 12 miles northeast of the plant.

All five samples were analyzed by SSMS (Table 1); each of the three sample types (ash, water, and grass) required a different preparation technique. The two ash samples, which were black, oily substances of relatively low density, were weighed and heated in a muffle furnace at 500° C for six hours to remove the organic components. The residue was dissolved in nitric acid, and yttrium was added as an internal standard. The two water samples were spiked with yttrium and dried onto graphite electrodes. The grass

Table 1. ELEMENTS DETECTED BY SSMS IN PLANT YARD ASH AND RELATED SAMPLES

Element	Ash From Plant Yard, µg/g	Airborne Ash Found Northeast of Plant µg/g	Roadside Water Collected Northeast of Plant, µg/l[a]	Lake Lugert Water Sample, µg/l[a]	Grass Leachate, µg/g	Ashed Grass, µg/l
Ca	22,000	1,000	23,000	50,000	5,000	90
P	7,000	140	50	2	200	3
Si	7,000	800	N.R.[b]	N.R.[b]	N.R.[b]	40
K	2,000	230	700	3,000	1,500	20
As	1,400	1,000	2	2	0.5	0.1
Na	900	500	19,000	21,000	200	N.D.[c]
Al	800	100	12	2	100	3
Zn	500	76	0.7	4	9	0.2
Fe	300	250	48	50	60	6
Cl	90	70	650	4,000	300	1
Mg	90	18	250	900	200	N.D.[c]
S	70	16	19	90	N.D.[c]	16
Mn	30	8	6	4	17	2
La	15	N.D.[c]	N.D.[c]	N.D.[c]	1	N.D.[c]
I	13	N.D.[c]	0.5	0.4	0.3	N.D.[e]

[a] Average of duplicate analyses

[b] Not reported; glassware used in sample preparation

[c] Not detected; less than 0.1 µg/g

sample was leached with acetone and with nitric acid; combined leachates were spiked with yttrium, dried onto graphite, and heated at 500° C for six hours. Leached grass blades were ashed at 500° C for six hours; the residue was dissolved in nitric acid, spiked with yttrium, and dried onto graphite.

Both ash samples contained high concentrations of arsenic and phosphorus (Table 1). All 15 elements detected in the plant yard ash were also found in the airborne ash, except lanthanum and iodine, which were the two elements present in lowest concentrations in the yard ash. Several elements (Sb, Ba, F, V, Br, Cu) were found in the airborne ash but not in the plant yard ash; the only one of these present in significant concentration in the airborne ash was antimony (130 μg/g). Its presence in the airborne ash could be explained because of its use in paints and enamels as a flame-proofing agent, but its absence in plant yard ash was puzzling.

SSMS analysis of the grass and water samples did not reveal appreciable contamination that could be directly related to the pesticide plant explosion and fire. The phosphorus and aluminum contents of these samples could possibly have been related to the incident, but none of the samples contained appreciable amounts of arsenic. The roadside water sample contained some black oily material that appeared to be the same as the ash samples, but not enough was present to cause significant water contamination. Mercury was not detected by SSMS, but it could have been lost during sample preparation procedures.

Ash samples were also analyzed by neutron activation to confirm arsenic concentrations determined by SSMS and to determine mercury concentrations. NAA confirmed high concentrations of arsenic in both ash samples; mercury was detected in the plant yard ash but not in the airborne ash (Table 2). Appreciable amounts of phosphorus in the ash samples produced energetic beta emissions that interfered with determination of ^{197}Hg. Therefore, values for the ^{203}Hg isotope, which has a lower relative activity, were also reported. The interference of antimony with the primary photon of ^{76}As dictated acquisition of data for both its primary photon with an energy of 559.1 keV and its 657.1 keV photon.

Results of SSMS and NAA analyses were reported to the EPA's Region VI Surveillance and Analysis Division, who included these data in a report that included results of mercury analysis by flameless atomic absorption and organic pesticide residue analyses by gas chromatography (GC) and

Table 2. MERCURY AND ARSENIC IN ASH SAMPLES ANALYZED BY NEUTRON ACTIVATION

Element	Ash From Plant Yard, µg/g[a]	Airborne Ash Found Northeast of Plant, µg/g[a]
^{197}Hg	8	N.D.[b]
^{203}Hg	11.3	N.D.[b]
As(559.1 keV)	1160	775
As(657.1 keV)	1280	628

[a] Average of duplicate determinations

[b] Not detected; less than 0.1 µg/g

combined gas chromatography-mass spectrometry (GC-MS). In their report to the Oklahoma State Health Department, they concluded that ash and debris from the plant fire did not cause a critical environmental hazard. Although ash collected from the plant yard contained potentially dangerous amounts of toxic substances, most ash was confined to the yard. This ash was collected and buried in a clay formation where leaching into surface and ground water was unlikely to occur. The airborne ash also contained significant quantities of arsenic but the low density of the material reduced its environmental hazard. Evidence for this conclusion was the low arsenic content (2 µg/l) of an obviously ash-contaminated water sample (the roadside sample). This is well below the proposed maximum acceptable arsenic concentration of 100 µg/l in drinking water.[4]

2. CHEMICAL ELEMENTS IN WATER FROM SUGAR BEET WASTEWATER HOLDING PONDS

As part of a study of possible ground water contamination from wastewater holding ponds, the SERL was asked to analyze several water samples by SSMS. The EPA's National Field Investigations Center (NFIC) in Denver, Colorado, needed elemental analyses to determine the extent of ground water contamination by sugar beet processing plant wastes. To conform to pollution control guidelines, by 1977 the industry must use holding ponds for all liquid wastes and discharge no liquids to receiving waters. Some holding pond liquids percolate through the soil and into ground water, constituting a potential source of pollution. The SERL was asked to analyze samples from holding ponds and ground water sources to determine whether significant differences in trace metal content existed. If such differences exist, characteristic elements could be monitored to enforce pollution guidelines.

Seven samples (three holding pond water samples, three upstream ground water samples, and one downstream ground water sample) from Colorado, Kansas, and Nebraska were collected, preserved with nitric acid, and shipped in nitric-acid cleaned glass bottles. For SSMS analysis, an aliquot of each filtered sample was dried onto graphite electrodes.

SSMS data (Table 3) indicated that phosphorus was the element most likely to be characteristic of ground water pollution by sugar beet wastes in holding ponds, but more data are needed to justify this hypothesis. Only two

Table 3. ELEMENTS DETECTED IN HOLDING POND AND GROUND WATER SAMPLES

Element	Kansas Samples		Colorado Samples		Nebraska Samples		
	Holding Pond Water, µg/l[a]	Upstream Ground Water, µg/l[a]	Holding Pond Water, µg/l[a]	Upstream Ground Water, µg/l[a]	Holding Pond Water, µg/l[a]	Upstream Ground Water, µg/l[a]	Downstream Ground Water, µg/l[a]
Ca	50,000	1,000	>10,000	3,000	≥10,000	≥40,000	≥10,000
K	10,000	100	> 3,000	300	≥ 2,000	1,000	≥ 1,000
Sr	9,000	180	400	400	106	1,600	250
Ba	4,800	20	60	40	30	1,200	400
Fe	3,400	1	2,300	400	60	160	12,000
Mg	1,600	2,000	1,100	900	≥ 900	2,000	800
Mn	1,300	0.5	250	16	220	2	1,400
P	> 1,000	1	160	1	≥ 2,000	1	4
Al	500	1	500	140	310	30	2
I	400	1	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]
Sn	250	N.D.[b]	N.D.[b]	N.D.[b]	0.6	N.D.[b]	0.2
Ce	200	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]
Pb	160	0.5	150	200	50	70	30
Cr	160	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]
Ni	100	2	N.D.[b]	N.D.[b]	25	N.D.[b]	N.D.[b]
Cu	60	0.1	20	200	5	1,400	5
S	50	1	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]
Zn	40	20	20	30	35	250	150
La	30	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]
Ag	2	1	4	2	1	N.D.[b]	0.5
Br	N.D.[b]	N.D.[b]	40	90	10	25	10
Co	N.D.[b]	N.D.[b]	10	2	N.D.[b]	N.D.[b]	N.D.[b]
Ga	N.D.[b]	N.D.[b]	6	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]
V	N.D.[b]	N.D.[b]	4	2	3	4	1
Sn	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	1	N.D.[b]	N.D.[b]
Zr	N.D.[b]	N.D.[b]	N.D.[b]	N.D.[b]	0.7	N.D.[b]	N.D.[b]

[a] Average of duplicate analyses

[b] Not detected; detection level is 0.5 µg/l

elements, phosphorus and aluminum, were present in higher concentrations in all three holding pond samples than in upstream and downstream samples. Differences in phosphorus concentrations were more significant than those for aluminum.

In Kansas samples, all elements detected, except magnesium, were present in the holding pond sample in greater concentrations than in the upstream ground water sample. Magnesium concentrations were approximately equal in both samples. However, the Nebraska upstream water sample contained larger amounts of calcium, strontium, barium, magnesium, zinc, and copper than either holding pond water or downstream water. In Colorado samples, more copper was present in upstream water than in wastewater.

These data were reported to NFIC officials who compared them with results of other analyses performed by other laboratories. Analytical data indicated that no serious pollution problem had resulted from holding pond seepage.

3. CHEMICAL ELEMENTS IN WASTE PLATING SOLUTION

To plan a safe disposal method, the United States Army Medical Laboratory at Fort McPherson, Georgia, requested elemental analysis of a waste liquid that was thought to be a metal-plating solution. For about 20 years, approximately 600 gallons of this solution had been stored at Fort Stewart, Georgia, but information as to its former use and its contents was no longer available. The SERL was requested to analyze the solution for its elemental content and to determine if the suspected high concentrations of cyanide were present.

SSMS analysis revealed that the solution contained very high concentrations of cadmium along with significant amounts of iron and copper (Table 4). Relatively small 1-ml samples were spiked with yttrium as an internal standard and evaporated onto graphite electrodes. The small sample size was dictated by the high salt content of the solution. The use of a small sample raised the lower limit of detection to approximately 1 mg/l, but eliminated the need for extensive salt removal procedures.

At the SERL's request, personnel from the EPA's Region IV Surveillance and Analysis Division determined the cyanide concentration in the solution. Using colorimetric analysis

Table 4. ELEMENTS DETECTED IN WASTE PLATING SOLUTION

Element	Concentration, mg/ℓ[a]
Na	50,000
Cl	50,000
Cd	40,000
Fe	1,200
Cu	140
Mg	40
Mn	3

[a] Average of duplicate analyses

of the acidified sample, they found the cyanide concentration to be 28.5 g/l.

The high concentration of cyanide and cadmium dictated that careful disposal methods be devised to avoid hazardous environmental contamination. Fort Stewart officials decided that such a toxic solution required expert attention, and an experienced waste reclamation firm was hired to handle the disposal.

4. ELEMENTAL COMPOSITION OF A MAJOR COMPONENT OF ORE PROCESSING PLANT TAILINGS

Spark source mass spectrometric analysis provided information about the elemental composition of a silicate mineral thought to be the majcr component of tailings discharged from a Minnesota iron-ore processing plant. The EPA's National Water Quality Laboratory in Duluth, Minnesota, requested this analysis to assist in its investigation of the ecological effects of mine wastes dumped into Lake Superior. Each day the plant discharges a slurry containing approximately 60,000 long tons of taconite wastes; half of this is thought to be cummingtonite, a magnesium-iron silicate that comprises about 30% of the mine's raw ore. Since cummingtonite is discharged in such large quantities, even its trace metal components could be quite significant.

A pure sample of cummingtonite can be obtained only with extremely tedious procedures, and the literature contains conflicting reports of its composition. The cummingtonite sample sent to the SERL for analysis was a composite of hand-picked crystals that had been collected for use as a standard for X-ray analysis of lake water and sediment.

To obtain the best possible composite for SSMS analysis, the hand-picked crystals were combined and ground into a powder. A portion of the powder was spiked with yttrium as an internal standard. Two aliquots of this spiked sample were analyzed to provide quantitative data for the major elemental components. The aliquots were then diluted with unspiked cummingtonite to obtain quantitative data for minor components.

The cummingtonite sample contained so much silicon that no attempt was made to quantify it, but quantitative data were obtained for seven other major components (Table 5) and 15 minor components (Table 6).

Table 5. MAJOR ELEMENTAL COMPONENTS OF CUMMINGTONITE

Element	Concentration Weight Percent[a]
Fe	1.6
Ca	1.6
Mn	0.4
Mg	0.1
Na	0.1
Cl	0.03
F	0.01

[a] Average of duplicate analyses

Table 6. MINOR ELEMENTAL COMPONENTS OF CUMMINGTONITE

Element	Concentration, μg/g[a]
K	100
Al	30
P	10
Cr	10
Sb	10
Cu	10
La	10
Ba	4
V	4
Br	2
Tm	2
Pr	2
Cs	2
Pb	1
Co	2

[a] Average of duplicate analyses

These data were reported to the National Water Quality Laboratory for use in the continuing evaluation of environmental effects of the mineral processing wastes.

5. CHEMICAL ELEMENTS AND VOLATILE ORGANIC COMPOUNDS IN LANDFILL LEACHATE

To determine a practical treatment for water containing pollutants leached from an abandoned landfill, Delaware's Department of Natural Resources requested analyses of several water samples.

In a residential and light-industrial area of Newcastle County, Delaware, a resident complained about a persistent, unpleasant odor in his drinking water. Although the water was supplied by a private company, various governmental agencies became involved when the obnoxious odors were traced to contaminants leached from an abandoned landfill near the commercial wells.

For about 13 years, Newcastle County had used an abandoned sandpit as a receptacle for municipal and industrial garbage. In 1968, the landfill was closed after an area three miles long and varying from 0.25 to 0.5 mile wide was filled with refuse estimated to be 30 to 50 feet deep. Within one mile of the outer edge of the landfill is the Artesian Water Company's Well field, from which three to five million gallons of water are pumped daily.

Newcastle County hired a consulting firm to determine the pollution source and to propose a remedy to prevent further ground water contamination. The consulting engineers concluded that landfill leachate had polluted the aquifer. To prevent further contamination of the well field, the consulting firm proposed drilling recovery and blocking wells. Blocking wells would be located to remove water that would normally flow into the landfill area and be contaminated. Recovery wells would be drilled in or near the landfill area to remove the leachate-containing water, which could then be treated and returned to the aquifer. Only treated water would then reach the private well field. To monitor aquifer pollution and to devise an effective treatment, state and county officials needed knowledge of the chemical composition of the leachate. Therefore, Delaware's Department of Natural Resources requested through the EPA's Region III office in Philadelphia, Pennsylvania, that the SERL identify organic and inorganic pollutants in four water samples: water from a well inside the landfill,

water from two recovery wells between the landfill and the well field, and finished water from the Artesian Well Company (Figure 1).

Volatile organic components were identified and measured by gas chromatography and combined gas chromatography-mass spectrometry. Each sample was extracted by a procedure designed to separate it into neutral, acid, and basic fractions.[6] Preliminary examination by GC showed which fractions contained significant amounts of organic components, and mass spectral data were acquired for these fractions. Preliminary identifications of several compounds were obtained by computer-matching of unknown mass spectra with standard mass spectra in a data bank. When standard samples were available, these identifications were confirmed by comparing mass spectra obtained under the same conditions. Further confirmation was obtained by comparing GC retention times of standards and unknowns. Quantitative data were calculated from GC peak area measurements.

The relative contamination in each well was shown by comparison of the total amount of organic materials indicated by peak areas from the gas chromatograms. These data (Table 7) showed that the landfill well contained approximately 100 times more volatile organic matter than the recovery wells.

Thirty compounds were positively identified and quantitated in the landfill well sample (Table 8). Major components were short-chain ($\leq C_8$) acids and industrial chemicals. The most concentrated volatile organic component was 2,3-dibromo-1-propanol (23.8 mg/l). Several compounds (various alcohols, hydrocarbons, and ethers) that were tentatively identified could not be positively identified, because no standards were available. One of these was 1-chloro-2,3-dibromopropane, a derivative of the major organic contaminant of the well.

Several compounds (caprolactam and nine short-chain acids) were found in both recovery well #3 and landfill well water (Table 8). Although the major component of the landfill well, 2,3-dibromo-1-propanol, was not positively identified in water from recovery well #3, GC evidence suggested that a trace amount of this compound was present.

Recovery well #29 was less contaminated than recovery well #3, but several compounds were identified: triethyl phosphate, mono- and dichlorobenzene, and eight short-chain acids (Table 8). Seven of the acids were also found in well #3.

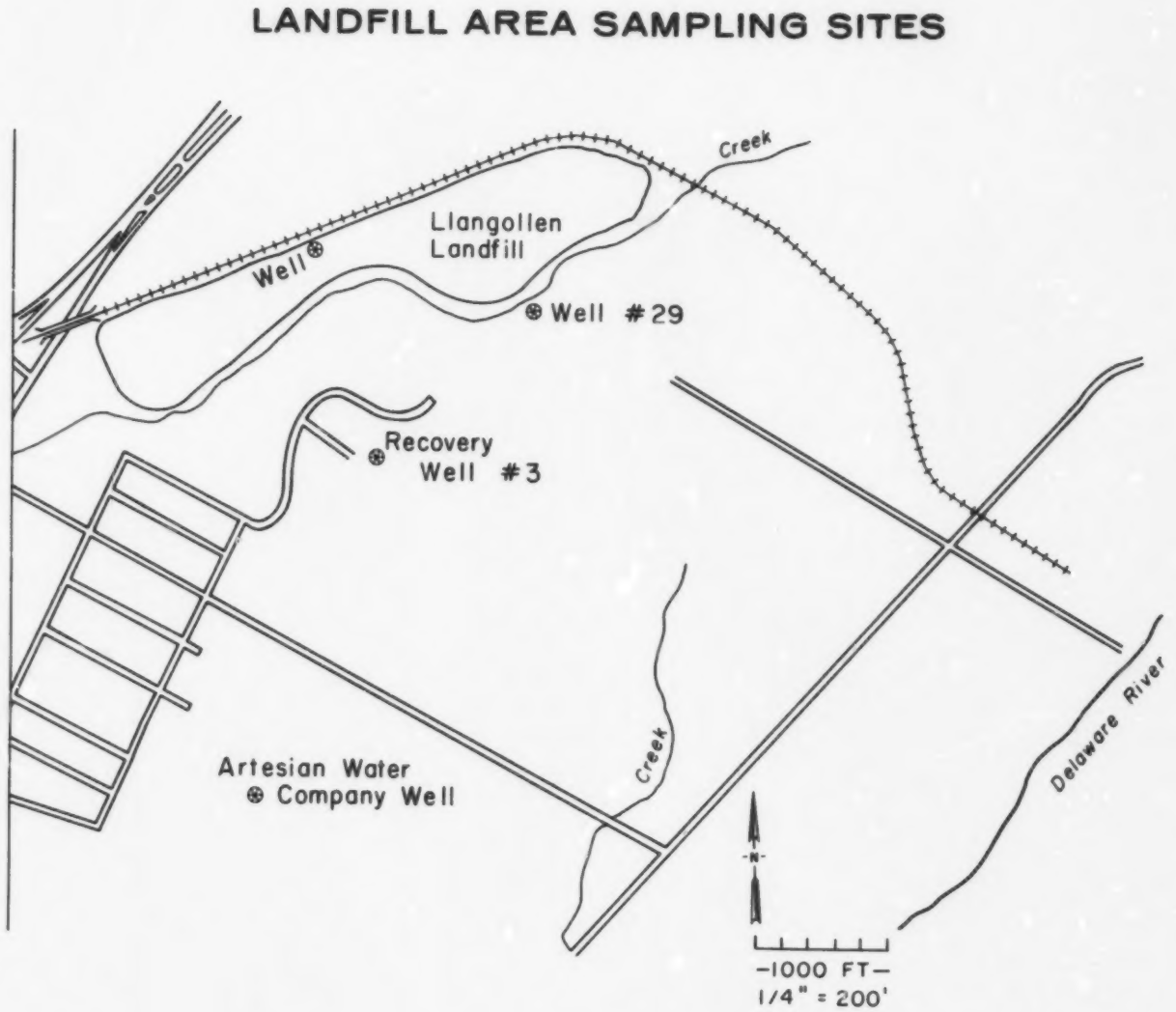

Figure 1. Sampling sites for landfill leachate analyses

Table 7. VOLATILE ORGANIC MATERIAL IN WELL WATER SAMPLES

Sample	Concentration, mg/ℓ[a]
Landfill Well	89.3
Recovery Well #3	1.5
Recovery Well #29	0.4
Artesian Water Co. Well	0.005

[a] Calculated from area of major portion of gas chromatogram.

Table 8. VOLATILE ORGANIC COMPOUNDS IDENTIFIED IN WELL WATER SAMPLES FROM LANDFILL AREA

Compound	Landfill Well Extract Concentration, mg/l[a]	Recovery Well #3 Extract Concentration, mg/l[a]	Recovery Well #29 Extract Concentration, mg/l[a]	Detection Thresholds in Water, mg/l[b]	
				Taste	Odor
n-butanol	5.4			0.5	2.5
camphor		0.007		1.9	
caprolactam	3.0	0.03[c]			
chlorobenzene			0.03[c]		0.07- 0.65
o-cresol		0.03			
p-cresol		0.16			3.5
cyclohexanol		0.005[c]			
diacetone alcohol	2.9				
2,3-dibromo-1-propanol	23.8		0.07		
dichlorobenzene					
diethyl phthalate	1.2				270
2-ethyl hexanol	0.2[c]				
fenchone	0.2[c]				
1-methoxy-2-propanol	0.3[c]				0.02- 0.03
phenol	9.9	0.005[c]			
1,4-thioxane			0.01		
triethyl phosphate					2.2
p-xylene	0.1[c]		0.19	20-40	2.4
acetic acid	4.7	0.3			
benzoic acid	2.4	0.02[c]	0.03	6.2-6.4	<17
butyric acid	39	0.004	0.005		3
heptanoic acid		0.03	0.01	2.5-50	3
hexanoic acid	5.9		0.005	1.6	8.1
isobutyric acid	1.3	0.07	0.005		0.7
isovaleric acid	0.6	0.24		5.8	3
octanoic acid	2.6		0.005		20
phenylacetic acid		0.07[c]			
propionic acid	6.5	0.09	0.005		3
toluic acid	0.1				
valeric acid	0.5	0.03			

[a] Because extraction efficiencies are unknown, reported concentrations are minimum values.

[b] From Compilation of Odor and Taste Threshold Values Data, Edited by W. H. Stahl, Amer. Soc. for Testing and Materials, Philadelphia, PA, 1973.

[c] Estimated value; not as accurate as unqualified concentrations.

The Artesian Well Company water extract did not contain volatile organic contaminants in quantities that could be detected by GC or GC-MS, and no organic compounds were identified. The neutral-fraction chromatogram showed only a few ill-defined humps with no sharp peaks; the acid-fraction chromatogram had no peaks. Compounds present in this finished water at concentrations ≥0.001 mg/l should have been detected, because the finished water extract represented a larger sample volume than the well water extracts.

SSMS analysis produced quantitative data for the 21 elements detected (Table 9) in these four samples and supported the volatile organic component analyses. The landfill well sample was the most contaminated; well #29 was less contaminated than well #3. Several elements were present in considerably higher concentrations in the landfill well water than in other water samples, but the most significant differences were observed for concentrations of bromine and barium. The high concentration of bromine in the landfill well supported the identification of 2,3-dibromo-1-propanol as the major organic contaminant. Comparison of SSMS data from all four samples indicated that magnesium, iron, manganese, cobalt, and boron would be other useful elements to trace the movement of contaminants from the landfill toward the well field.

Analytical data were reported to the Delaware Department of Natural Resources. A series of recovery wells has been completed. Water from these wells is presently discharged into small creeks in the area, but the county is constructing aeration tanks that will permit effluent discharge into a tidal area beyond the freshwater zone.

6. TASTE AND ODOR PROBLEMS IN WELL WATERS

a. Municipal Well

For over a year, citizens of the small town of Milner, Georgia, complained about an unpleasant odor in their drinking water. The odor was similar to that of natural gas to which an odorous material has been added to permit rapid detection of leaks during shipping or use. Townspeople suspected that the source of the odor was a nearby cavern that was used for propane storage. Leachate from the storage cavern could have contaminated the aquifer feeding

Table 9. ELEMENTS DETECTED IN WELL WATER SAMPLES FROM LANDFILL AREA

Element	Concentration, µg/l[a]			
	Landfill Well	Recovery Well #3	Recovery Well #29	Artesian Water Company Well
Mg	28,000	11,000	4,800	155
Br	10,700	66	26	6
Fe	8,800	8,800	2,500	139
Ca	7,200	4,900	1,400	2,200
Cl	5,200	2,000	2,000	1,900
K	3,300	2,100	900	1,200
Ba	2,600	366	340	42
S	1,800	1,400	120	48
Mn	1,400	1,800	490	10
Sn	900	106	22	26
Rb	327	22	6	4
B	256	36	28	0.2
F	182	84	66	8
P	145	74	5	7
Al	116	168	70	26
Zn	68	38	14	6
Cr	60	23	8	N.D.
Cu	39	2	0.3	8
Co	30	139	26	0.4
Pb	4	N.D.	N.D.	2
I	N.D.	2	N.D.	N.D.

[a] Average of duplicate analyses

the deep well that supplies the town's water. However, the cavern had been used for propane storage for ten years, and pipeline company officials reported that ethyl mercaptan is added to the propane when it is shipped, not before or during storage.

The Georgia State Department of Natural Resources requested assistance in locating the contamination source. The SERL examined samples of water from the cavern, from the town well, from a well located between the cavern and the town, and from a well located several miles on the opposite side of town. The town well water and cavern water samples had similar odors, but the cavern water odor was stronger.

Town well and cavern water both contained some sulfur compounds and other organic impurities, but different compounds were present in each sample. None of the samples contained ethyl mercaptan at ≥50 µg/l, the detection limit with the analytical method used. The odor component of each sample was concentrated in a steam distillate, which was placed in a sealed vial from which the headspace gas could be sampled with a syringe. Headspace gases were analyzed with a gas chromatograph equipped with a flame photometric detector (FPD) that responds almost exclusively to sulfur-containing compounds. The cavern water sample contained four sulfur compounds. The concentration of the major one was estimated to be 4 mg/l; the other three were present at much lower concentrations. Water from the town well and from the well between the town and the cavern contained the same single sulfur compound, which was not present in the cavern water.

The steam distillates were also examined by direct injection into a combined GC-MS. The town water sample contained at least one organic contaminant and the cavern sample contained more than two. None of these contaminants contained sulfur, and the town well contaminant was not present in the cavern sample. These compounds could not be specifically identified from their weak mass spectra.

Methylene chloride and tetradecane extracts of the town water sample did not contain any impurities detectable with the GC (FPD), and the odor remained in the water after the attempted extraction. In a control experiment, the mercaptan odor was easily discernible in a solution containing 15 ug ethyl mercaptan per liter water, but attempts to remove the mercaptan by conventional methods were unsuccessful.

Hydrogen sulfide was eliminated as a possible odor-causing pollutant; a sulfide specific-ion electrode showed clearly

that hydrogen sulfide concentration was less than 1 ng/l (1 ppt).

No evidence was found to link the town water contamination to leachate from the storage cavern. Both samples could have contained ethyl mercaptan at a level that could have caused an objectionable odor but would not have been detected. However, the lack of similarity in other organic compounds found in the two samples led to the conclusion that the source of contamination was probably not the cavern.

Later, independent analyses supported the lack of evidence connecting the cavern with town well contamination. Town well and cavern water samples were collected and shipped to the EPA's Methods Development and Quality Assurance Research Laboratory in Cincinnati, Ohio, for analysis. Volatile organics were removed by bubbling nitrogen gas through each sample and into a small column packed with a porous polymer that trapped the organics.[7] The trapping column was placed in a GC injection port where the volatile organics eluted into a standard column for GC and GC-MS analysis. Dimethyl ether, acetone, methanol, and isopropanol were present in high concentrations in the cavern water but were absent from the town water. This strongly indicated that the cavern was not the contamination source. If contaminated water moving from the cavern to the town well were causing the odor problem, these four very water-soluble compounds should be present in town well water. No ethyl mercaptan was detected, but its detection limit with this purging-trap method was judged to be as high as 100 µg/l.

After these analyses and other tests performed by the Georgia State Water Laboratory and by a private consulting laboratory failed to identify the odorous contaminant or its source, the townspeople decided to abandon their inadequate and odorous well and obtain water from a nearby town's water system.

b. Private Well

A similar problem involved the unpleasant taste of water from a 300-ft deep sealed well in a non-industrial and lightly populated area in Georgia. Industrial contamination of the aquifer seemed unlikely, and no probable pollution source could be located.

Examination of well water extracts (carbon tetrachloride) by GC and GC-MS revealed the presence of long-chain, normal hydrocarbons (C_{21}-C_{31}). Since such long-chain materials are

not found in fuel or lubricating oils, the pollutant was suspected to be a lubricating wax leaking from the submerged pump. Indeed, the taste problem disappeared when the pump was replaced.

7. VINYL CHLORIDE IN WATER

a. Analytical Method

A cursory investigation of the behavior of vinyl chloride in water solutions revealed that the volatility of vinyl chloride makes it a much greater threat as an air pollutant than as a water pollutant. The occurrence of a rare type of tumor in certain industrial workers was thought to be related to their occupational exposure to vinyl chloride. The EPA Administrator appointed a task force to advise him of the Agency's best course of action to determine the significance of vinyl chloride as an environmental pollutant. To assist this task force, the EPA's Office of Monitoring Systems requested assistance from several EPA laboratories. The SERL's Analytical Chemistry Branch was asked to provide information about methods for quantitative analysis of vinyl chloride in water. Assessment of existing methods and, if necessary, development of new methods were needed within the month before the first task force meeting.

Two gas chromatographic methods for analysis of vinyl chloride in aqueous solutions were shown to be reproducible and quantitative at mg/l concentrations. The detection level with the previously-developed method of direct aqueous injection (2 µl) varied from 0.05 to 2 mg/l, depending on the condition of the particular gas chromatograph used. Samples containing lower vinyl chloride concentrations required solvent (carbon tetrachloride) extraction. A detection level of approximately 2 µg/l was attained with a 2-µl injection of carbon tetrachloride extract. Four effluent samples from a plastics manufacturing plant were analyzed with both techniques; data indicated that either method was applicable for the concentrations (0.2-9.3 mg/l) of vinyl chloride found in these samples (Table 10).

The presence of vinyl chloride in the effluent samples was confirmed by GC-MS analysis. A 2- 1 (4 ng) direct aqueous injection of the 0.2 mg/l samples produced a good mass spectrum, and an acceptable spectrum was obtained from a 2-µl injection of a carbon tetrachloride extract containing 0.14 ng of vinyl chloride.

Table 10. VINYL CHLORIDE IN INDUSTRIAL EFFLUENT SAMPLES

Sample	Vinyl Chloride Concentration, mg/ℓ	
	Direct Aqueous Injection	CCl_4 Extraction
Primary Clarifier Effluent[a]	2.8	3.0
Primary Clarifier Effluent[a]	2.8	2.9
Primary Clarifier Scum[b]	9.3	6.8
Plant Storm Sewer Effluent	0.2	0.2

[a] Samples taken on two different days.

[b] Sample contained large amount of suspended particulates.

A major problem with analysis of vinyl chloride in aqueous solutions is its volatility. Because aqueous solutions are not stable, carbon tetrachloride solutions were used to calibrate the flame ionization detector in both GC methods. This volatility also necessitates careful sample collection, shipment, and storage. However, it does permit headspace-gas analysis[8], which is a rapid and sensitive method for screening water samples for vinyl chloride.

b. Loss Mechanisms

A brief study of the behavior of vinyl chloride in aqueous solutions indicated that the most important loss mechanism is volatilization rather than hydrolysis or photolysis. The volatilization rate varied with agitation rate. During two hours of rapid stirring at 22° C, a 16 mg/l solution of vinyl chloride in distilled water lost 96% of the solute; a quiescent solution of the same concentration lost 25% under the same conditions. No significant rate differences were observed for vinyl chloride loss from distilled water, river water, or industrial plant effluent, indicating negliglible adsorption of vinyl chloride by particulate matter. When the industrial plant's clarifier effluent was spiked with 110 mg vinyl chloride/l effluent and stirred rapidly for three hours, the vinyl chloride concentration decreased to 21.8 mg/l. Under the same conditions, river water and distilled water solutions decreased from 105 mg/l to 2.2 mg/l and 1.8 mg/l, respectively.

The loss of vinyl chloride from clarifier effluent samples was not affected by pH variations. During 57 hours at 50° C, vinyl chloride concentrations decreased at the same rate in solutions of pH 4.3, 8.0, and 9.4. This lack of pH dependence suggested loss by volatilization rather than by hydrolysis.

Another experiment eliminated sunlight-induced photolysis as an important mechanism for vinyl chloride loss from aqueous solutions. Relative to a shielded blank, vinyl chloride concentration did not decrease in industrial plant effluent exposed to sunlight during a 57-hour period (approximately 25 hours of sunlight).

This information was presented to the EPA Vinyl Chloride Task Force. After receiving data from several laboratories, the task force recommended that the EPA's concern and action should be directed at vinyl chloride as an air pollutant. Data indicated that no further laboratory studies of vinyl chloride were justified at that time.

8. DISSEMINATION OF ANALYTICAL INFORMATION

The ACB's analytical expertise was utilized by scientists in industry, universities, and state and federal agencies. Requests were answered for publication reprints, standard samples, analytical methods, monitoring procedures, and information about previously identified wastewater components.

a. Consultations

- Continued interest in the GC method[9] for identification and quantitation of polychlorinated biphenyl (PCB) isomers prompted more than a dozen requests for standard samples in FY 1974. Standards were provided to various analysts quantitating individual components of complex PCB mixtures in industrial effluents.

- A computer program[10], developed at Battelle Columbus Laboratories under an EPA grant, was provided to various people involved with GC-MS analysis of organic compounds. This program is used for selected-ion monitoring of organic compounds by computer-controlled GC-MS (quadrupole) systems. It enhances detection of specific compounds in complex mixtures and alleviates background interferences. Current applications range from effluent monitoring to detecting drug residues and metabolites in overdose victims.

- The ACB's knowledge of various industrial wastewaters was invaluable to contractors who are compiling industrial effluent guidelines and performing effluent analyses to support these guidelines. ACB personnel provided advice about advanced analytical instrumentation and techniques for analysis of water pollutants.

- To evaluate proposed textile effluent guidelines and grant proposals to study wastewater treatment methods, the SERL's Industrial Pollution Branch utilized the ACB's knowledge of textile industrial effluents. The ACB provided information about water consumption by various dyeing processes and advice about proposed treatment facilities for printing wastewaters.

b. Symposium

In April, 1974, the Symposium on the Identification and Transformation of Aquatic Pollutants, was planned and coordinated by SERL personnel from the ACB and the Freshwater Ecosystems Branch. This symposium was designed to provide a forum for chemists to learn about pollutant transformation processes and products and for biologists to learn of recent developments in analytical techniques, instrumentation, and methods. Invited speakers presented technical talks equally balanced between biological and chemical aspects of water pollution. Emphasis was placed on state-of-the-art discussions including examples of recent research results that had not been published or might not have attracted the attention of workers not involved in that particular field.

The symposium, held in Athens, Georgia, was jointly sponsored by the EPA, the American Chemical Society, the American Society for Microbiology, and the University of Georgia. Industrial, academic, and governmental institutions were equally represented by the 303 participants from 41 states and 4 foreign counties.

SECTION IV

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SECTION V

GLOSSARY OF ABBREVIATION

ACB - Analytical Chemistry Branch

EPA - U. S. Environmental Protection Agency

GC - gas chromatography

GC-MS- combined gas chromatography and mass spectrometry

MS - mass spectrometry

NAA - neutron activation analysis

NFIC - National Field Investigations Center of the Environmental Protection Agency

PCB - polychlorinated biphenyl

SSMS - spark source mass spectrometry